

Center Reflections

A monthly publication highlighting activities at the W.M. Keck Foundation Center for Molecular Structure

California State University Fullerton

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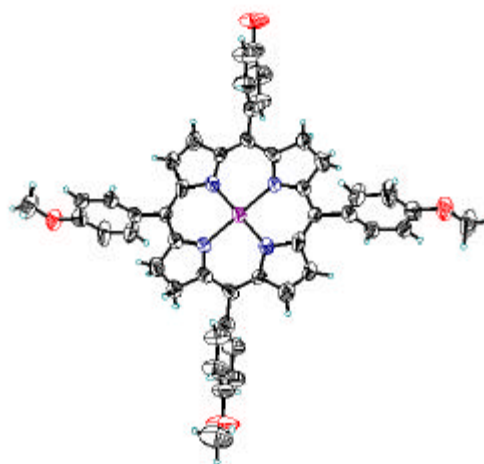
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Synthesis and Characterization of Platinum(IV) Complexes of Tetraphenylporphyrin (TPP) Ligands

CSU San Bernardino

The research being undertaken by Prof. John Tate at CSU San Bernardino involves the coordination chemistry of transition metal ions with large polydentate ligands. Tate has interests in the areas of the coordination chemistry of biological molecules and of coordination compounds displaying interesting magnetic properties. Knowing the exact three-dimensional structure of these compounds is essential to understand their physical properties such as magnetism, and electronic spectra.

In 1998, Tate spent his sabbatical at CMoIS learning x-ray diffraction methods and how to use the instruments and software to carry out a structure determination. He determined the structure of two platinum porphyrins for Prof. Larry Mink, a colleague at CSUSB. One of these structures is of a platinum (IV) tetra(p-methoxyphenyl porphyrin) dibromide, believed to be the first x-ray structure of a platinum (IV) porphyrin complex. This structure is the subject of a paper being submitted to *Inorganic Chemistry*. The other structure is of the Pt(II) complex of the same ligand. The ORTEP of that structure is shown at the right.



Mink's research involves the synthesis and characterization of platinum(IV) complexes of tetraphenylporphyrin (TPP) ligands. Iron porphyrins have been used extensively in modeling the reversible oxygen storage function of myoglobin, the transport function of the hemoglobin proteins, and the reversible one-electron transfer of the cytochromes b and c. Porphyrin-like structures assume important roles in the absorption of sunlight by chlorophylls and the subsequent photosynthetic conversion. Transition metal TPPs have proven as effective catalysts in a variety of photoisomerization and oxidative dehydrogenation processes. Catalytically active metals are of the d^6 , d^7 and d^8 electronic configuration, in particular Fe(II), Co(II), Ni(II) and Pt(II). Catalytic activity is dependent on the central

metals, as well as on the substituents in the para positions of the phenyl ring in TPP. In particular, platinum and palladium porphyrins have been investigated as potential photosensitizers capable of photochemical conversion and storage of solar energy, as molecular conductors, as photosensitizers in *cis* to *trans* isomerization of stilbene, and in electrophilic substitution involving mercuration of the porphyrin ring. Mink and his students have succeeded in preparing the dichloro and dibromo platinum(IV) TPP, and they have grown very well formed single crystals of these complexes. Structures of the complexes are needed to confirm coordination environment around the metal. In particular the conformation of the porphyrin ring might provide useful information about the potential reactivity of the complex. For example some porphyrin complexes have ruffled rings, as opposed to flat, leading to increased reactivity. Previous attempts to determine the structures of these complexes were unsuccessful, due in part to desolvation during transport to a diffractometer.

Previously at CSUSB, publications were held up due to limited access to adequate instrumentation. Tate is introducing x-ray diffraction methods into a Topics course at CSUSB. The course is modeled after one taught by Kantardjieff (480T). Students grew single crystals and determined the structure of their compound, and results were written up in publication format. Clearly the practical difficulties in teaching such a course would be prohibitive, if the facilities at CMoIS were not available. Students will grow crystals at CSUSB, collect diffraction data at CMoIS, and then transfer the data back to CSUSB, where the structure determination will take place. A copy of the structure solution software will be available in the new NSF funded Chemistry Computer Laboratory at CSUSB and data are transferred remotely via Internet from CMoIS to CSUSB. These upgrades to instrumentation and software would allow for a very exciting addition to the undergraduate research options at CSUSB.

John Tate received his Ph.D. in Inorganic Chemistry at the University of Sheffield, England under the direction of D.E. Fenton. He then completed postdoctoral research with C.A. Reed at the University of Southern California and with D.C. Bradley at Queen Mary College, London, England. Prior to joining the faculty at CSU San Bernardino in 1990, Tate was a lecturer in Chemistry at the University of Manchester, England, U.C. Riverside, and CSU San Bernardino. John is a member of the advisory board at CMoIS.

Larry Mink received his Ph.D. at U.C. Riverside in the area of organometallic chemistry. He completed postdoctoral studies at the University of Arizona at Tucson in the field of bioinorganic chemistry relating to metalloporphyrin systems. He has been on the faculty at CSUSB since 1993. His research student, Martin Neitzel, received first place for undergraduate research at the ACS Western Biotechnology Conference in 1995.

Allen D. Hunter: New CMoIS Advisory Board Member and Author of SHELXTL Lab Manual

Youngstown State University

Allen D. Hunter is a professor of chemistry at Youngstown State University. YSU is a predominantly undergraduate institution located in downtown Youngstown and is comparable to many schools in the Cal. State system. Thus, it enrolls about 14,000 students in its colleges of Arts & Sciences, Education, Engineering, Fine & Performing Arts, Health and Human services, and Graduate Studies. Most of its students are drawn from the five surrounding counties in Northeastern Ohio and Western Pennsylvania and while a growing proportion of students live on campus approxi-

mately 90% still commute daily from home. As at many other state supported urban universities, the majority of YSU students hold substantial outside employment, averaging 30 hours a week! YSU offers a diverse range of degree programs including AB and BS degrees in Chemistry, Biology, Environmental Studies, Geology, and Physics and MS degrees in Chemistry and Biology.

Allen is the founder and director of the YSU Structure Center, located in the YSU Chemistry Department. This center, the Center for Biomedical Environmental Research housed in the Biology Department, and other science labs house a particularly wide range of instrumentation for a MS level institution. For example, "research grade" chemical instrumentation includes: a 400 MHz NMR spectrometer (with PFG, VT, and 4 multinuclear probes), two Bruker P4 single crystal diffractometers (one having a multi wire area detector), and two GC-MS systems. These instruments are all used for both teaching and research and are accessible to off campus users. Indeed, there is no charge for users from other predominantly undergraduate schools for access to YSU's scientific instrumentation.

Allen is also the founder and director of the Advanced Diffraction Studies Consortium (ADSC), a group of over three dozen Ph.D., MS, BS, and two-year institutions, federal research labs, and companies centered in Northern Ohio and Western Pennsylvania. The ADSC is dedicated to the integration of diffraction methods into teaching and research at predominantly undergraduate research. In this and other ways, it is analogous to CMoIS and for this reason Allen has recently been appointed to the advisory board of CMoIS.

As one contribution to this mission, Allen has recently released a lab manual, *Allen Hunter's Youngstown State University*

X-Ray Structure Analysis Lab Manual: A Beginner's Introduction. This 275-page manual is designed to serve as a step by step introduction for novices who want to determine a molecular structure from single crystal data. It is optimized for users of Bruker's SHELXTL package under DOS but is also very useful for those using the NT or UNIX versions of this package or using the George Sheldrick's SHELXS and SHELXL packages. It is available at no charge from Allen (adhunter@cc.ysu.edu) as two .pdf files and may be freely reproduced for instructional use. It is expected that this manual will be updated regularly (e.g., quarterly) based on user comments and contributions.

Allen Hunter did his BS and Ph.D. degrees at the University of British Columbia and was a postdoctoral fellow at the Australian National University and the University of Alberta. He was an assistant professor at the University of Alberta from 1987 until 1992 when he moved to YSU. His training was as a synthetic organometallic chemist, but as the years have passed his research interests have changed and are now focussed on the synthesis of novel organofluorine and organometallic polymers, on the preparation and study of host-guest supramolecular compounds, and on X-ray diffraction analysis. Allen's homepage may be found at: <http://www.as.ysu.edu/~adhunter/index.html>

Undergraduate Helped to Develop an Experiment in Crystallography for the Physical Chemistry Laboratory

CSU Fullerton

John K. Phan was an undergraduate research student at the W.M. Keck Foundation Center for Molecular Structure (CMoS) at CSU Fullerton in 1997. Under the direction of Drs. Katherine Kantardjieff and Guy Crundwell, John learned how to use x-ray crystallography to determine chemical structures and examine how they are packed in crystalline lattices. He developed an experiment for the physical chemistry laboratory that has been implemented in the chemistry departments at seven CSU campuses. In this experiment, students determine the crystal structure of benzil [$C_{14}H_{10}O_2$] and some of its derivatives. John presented his work at the national meeting of the American Chemical Society in Las Vegas in 1997, and this experiment is in press in the *Journal of Chemical Education*.¹ John states, "My experience as a research assistant was very rewarding, because I had the chance to learn and work with instruments that are the cutting edge in technology for studying crystallography, such as the Bruker 3-circle CCD diffractometer."

After John completed his B.A. in Chemistry, he worked as a project environmental chemist for United Soil Engineer, Inc. (U.S.E., Inc.) located in Santa Clara, CA. As a project environmental chemist, he performed pH, moisture, and dry density analyses on different soil materials. He also inspected proposed industrial building sites for any hazardous waste products that may have contaminated the soil, such as by illegal dumping of chemical toxins and petroleum. Based on his data, John wrote hazard assessments, geotechnical investigation re-

ports, and recommendations on how to clean and stabilize proposed industrial sites prior to any construction.

John says he enjoyed working at U.S.E., Inc., because "I love going into the field and meeting very knowledgeable people everyday." He also states, "After working at CMoS, I gained valuable skills and knowledge that have enabled me to work for science industries for the better of our environment. Now, I'm back at CMoS once again and working with a very knowledgeable group of people and getting a B.S. in Biochemistry. CMoS is like one big family and I'm very proud to be a member of it."

1. Crundwell, G., Phan, J. and Kantardjieff, K. "An experiment in single-crystal x-ray diffraction in the physical chemistry laboratory." *J. Chem. Ed.* In press.

Upcoming Events

March 14-17, 1999: **West Coast Protein Crystallography Workshop**, Asilomar, Pacific Grove, CA.

March 19-20, 1999: **American Chemical Society Shortcourse** "Crystallography for Chemists", CSU Fullerton

March 20, 1999: **Southern California Undergraduate Research Conference in Chemistry and Biochemistry, SCAURCON99**, CSU Fullerton

March 21-25, 1999: **American Chemical Society National Meeting**, Anaheim, CA.

May 22-26, 1999: **American Crystallographic Association Annual Meeting**, Buffalo, NY.

August 4-13, 1999: **International Union of Crystallography Meeting**, Glasgow, Scotland.

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